

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **09-217292**

(43)Date of publication of application : **19.08.1997**

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(51)Int.Cl.

**D21H 17/67**

**D21H 27/00**

**// C01F 11/18**

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(21)Application number : **08-016867**

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(22)Date of filing : **01.02.1996**

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## (54) **CALCIUM CARBONATE-FILLED PAPER**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a calcium carbonate-filled paper excellent in optical characteristics such as opacity and whiteness, good in balance of the optical characteristics with physical characteristics such as tensile strength and paper body strength, further capable of adjusting the extent of the above balance, having a high quality and inexpensive.

**SOLUTION:** This calcium carbonate-filled paper contains 5-35 pts.wt. calcium carbonate mixture of a spindle shaped calcium carbonate and a pillar-shaped calcium carbonate based on 100 pts.wt. bone dry weight of a raw material pulp. The weight ratio of the spindle-shaped to a pillar-shaped is preferably (95:5)-(40:60). Further, based on 100 pts.wt. bone dry weight, 5-35 pts. mixture of calcium carbonate consisting of (95:5)-(40:60) weight ratio of the spindle-shaped to the pillar-shaped calcium carbonate and 0.1-10 pts.wt. titanium oxide are preferably contained.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention excels [ this invention ] in optical properties, such as opacity and a whiteness degree, and Such an optical property, Balance with physical characteristics, such as tensile strength and nerve of paper, is good, It is a thing about quality and inexpensive calcium carbonate printing paper which can furthermore adjust the grade of this balance, Coating stencil paper [ like art paper and coat paper ] in which this thing is, and a PPC sheet, a thermal paper, As non-coating print sheets, such as office-use papers, such as an impact paper, hot printing paper, inkjet printing paper, electrostatic recording paper, and magnetic recording paper, upper printing paper, middle-class printing paper, and industrial use crossbred paper, It is suitably used as the back carbon paper which is easy to produce especially the performance difference of an inner filler, an Indian paper, or rice paper.

[0002]

[Description of the Prior Art]In the field of tissue paper, such as back carbon paper, an Indian paper, and rice paper, in order to improve the opacity of paper, a whiteness degree, etc. from before, loading materials, such as calcium carbonate, a titanium dioxide, and calcination clay, have been used. And about calcium carbonate, since the opacity of the tissue paper which inner-\*(ed) it is related to the particle shape and dispersibility, the thing of various particle shape is proposed according to the purpose of use.

[0003]For example, opacity is improved using pillar-shaped calcium carbonate, the amount of other loading materials used, such as a titanium dioxide and calcination clay, is reduced, and making the cost of tissue paper cut down is proposed (JP,S57-71499,A, JP,S62-282099,A).

[0004]However, since pillar-shaped calcium carbonate has the fault that reduce the stiffness of tissue paper, and a manufacturing process is complicated and a manufacturing cost increases rather than the case where spindle-shaped calcium carbonate is added, compared with spindle-shaped calcium carbonate and also when this is added, Although the opaque insufficiency is using together and compensating a titanium dioxide and calcination clay with usual tissue paper using spindle-shaped calcium carbonate, since it is necessary to increase the amount of concomitant use for acquiring necessary physical properties, the actual condition does not escape becoming a high cost.

[0005]

[Problem to be solved by the invention]Even if this invention is a basis of such a situation and it reduces the amount of concomitant use also by using together neither a titanium dioxide nor calcination clay, The outstanding optical properties, such as opacity and a whiteness degree, are shown, and Such an optical property, Balance with physical characteristics, such as tensile strength and nerve of paper, is good, and is made for the purpose of providing the quality and inexpensive calcium carbonate printing paper which can adjust the grade of this balance further.

[0006]

[Means for solving problem]The result of having repeated research wholeheartedly in order that this invention persons might develop the calcium carbonate printing paper which has the above mentioned good characteristic, By using as a loading material what added further a small amount of titanium dioxides to this mixture by the mixture of pillar-shaped calcium carbonate and spindle-shaped calcium carbonate, and the case, it finds out that that purpose can be attained and came to make this invention based on this knowledge.

[0007]That is, this invention provides the calcium carbonate printing paper per the oven-dry-weight 100 weight section and containing five to calcium carbonate mixture 35 weight section of spindle-shaped calcium carbonate and pillar-shaped calcium carbonate to a pulp raw material.

[0008]

[Mode for carrying out the invention]The pulp raw material of this invention can be arbitrarily chosen according to the purpose of use from the pulp usually used as a paper-making raw material. As such pulp, although cotton pulp, flax pulp, hemp pulp, paper mulberry, a paper bush, ganpi pulp, hemp-of-Manila pulp, straw pulp, bagasse pulp, various wood pulp, waste paper pulp, these mixed pulp, etc. can be mentioned, for example, Plants pulp and these mixed pulp, such as flax pulp, hardwood pulp, softwood pulp, and hemp pulp, are suitable for tissue paper. In this invention, the mixture of spindle-shaped calcium carbonate and pillar-shaped calcium carbonate is used as a combination ingredient to a pulp raw material.

[0009]Although the spindle-shaped calcium carbonate in particular used for this invention is not restricted, a major axis with SEM particle diameter 0.5-3.0 micrometers, It is preferred that a minor axis is 0.1-0.5 micrometer, the 50% accumulation particle diameter of laser type particle size distribution is 2.5-4.5 micrometers, 325 mesh-sieve passage residue is 0.005% or less, and a wire abrasion degree is 100 mg or less, and it is preferred that aspect ratios are 2-10 further. What makes calcite a subject is preferred, in addition, as for the thing of scalenohedron (scalenohedrons), a crystalline form is used. What comprises a calcite independent is included by what makes calcite a subject. The minor axis of the above-mentioned spindle-shaped calcium carbonate means the maximum width of a thickness direction.

[0010]Although any of an aragonite system and a calcite system may be sufficient as pillar-shaped calcium carbonate, this, In SEM particle diameter, a major axis is 0.5-3.0 micrometers, and a minor axis is 0.1-0.3 micrometer, It is preferred that the 50% accumulation particle diameter of laser type particle size distribution is 2.5-4.5 micrometers, 325 mesh-sieve passage residue is 0.005% or less, and a wire abrasion degree is 50 mg or less, and it is preferred that aspect ratios are 3-30 further. A thing [ that what makes aragonite a subject is preferred and it is needlelike (acicular) ] is also used. What comprises an aragonite independent is included by what makes aragonite a subject.

[0011]That it is advantageous especially as a calcium carbonate mixture used for this invention, In SEM particle diameter, a major axis is 0.5-3.0 micrometers, and a minor axis is 0.1-0.5 micrometer, The spindle-shaped calcium carbonate which the 50% accumulation particle diameter of laser type particle size distribution is 2.5-4.5 micrometers, 325 mesh-sieve passage residue is 0.005% or less, and a wire abrasion degree is 100 mg or less, and makes calcite a subject, In SEM particle diameter, a major

axis is 0.5-3.0 micrometers, and a minor axis is 0.1-0.3 micrometer, Aspect ratios are 3-30, the 50% accumulation particle diameter of laser type particle size distribution is 2.5-4.5 micrometers, 325 mesh-sieve passage residue is 0.005% or less, and a wire abrasion degree is 50 mg or less, and it is a mixture with the pillar-shaped calcium carbonate which makes aragonite a subject. As for this spindle-shaped calcium carbonate, it is preferred that aspect ratios are 2-10 further.

[0012]In the calcium carbonate mixture used for this invention, the suitable blending ratio of spindle-shaped calcium carbonate and pillar-shaped calcium carbonate is chosen the weight ratios 95:5 thru/or 40:60, especially within the limits of 80:20 thru/or 40:60. Rather than this, if the rate of spindle-shaped calcium carbonate increases, the wire abrasion degree in the case of paper milling will become high, and the opacity of the obtained paper will become low. As the combination method, where spindle-shaped calcium carbonate and pillar-shaped calcium carbonate are mixed beforehand, it can also add to a pulp raw material, and spindle-shaped calcium carbonate and pillar-shaped calcium carbonate can also be independently added into a pulp raw material.

[0013]It is necessary to a pulp raw material to blend preferably the blending ratio of the mixture of spindle-shaped calcium carbonate and pillar-shaped calcium carbonate at a rate of five to 30 weight section five to 35 weight section per the oven-dry-weight 100 weight section in this invention. If there are few these blending ratios than this, sufficient whiteness degree and opacity will not be acquired, and if more than this, cost will go up. In this invention, a titanium dioxide can be further used as a combination ingredient to a pulp raw material. It is necessary to a pulp raw material to blend preferably the blending ratio of the titanium dioxide in that case at a rate of 0.2 to 5.0 weight section 0.1 to 10 weight section per the oven-dry-weight 100 weight section. If there are few these blending ratios than this, a whiteness degree peculiar to a titanium dioxide and opacity will become insufficient, and if more than this, cost will go up.

[0014]Although it is a several time high cost as compared with calcium carbonate, since it excels in respect of opacity or a whiteness degree, the titanium dioxide is well used as a loading material ingredient for paper making. Although the amount used is variously changed by the kind of paper, a use, demand physical properties, etc., it is usually 10 to 30weight % of a range among all the loading materials. In this invention, even if it reduces the amount of the titanium dioxide used in 5 to 15weight % of the half in [above-mentioned] usual by using together pillar-shaped calcium carbonate and spindle-shaped calcium carbonate, physical properties equivalent to the usual case are acquired. This titanium dioxide can change that part into calcination clay by request.

[0015]In this invention, it is a range which does not spoil the original purpose other than these ingredients further, and various addition ingredients usually conventionally used for printing paper can be blended. As this addition ingredient, neutral size agents, such as a sizing compound, for example, an alkyl ketene dimer, an alkenyl succinic anhydride, neutral rosin, etc., Paper reinforcing agents, such as size fixing agents, such as yield improvers, such as acid sizing compounds, such as acid rosin and a petroleum system sizing compound, and polyacrylamide, cation starch, and a sulfuric acid band, and corn starch, are mentioned.

[0016]The calcium carbonate printing paper of this invention can be manufactured by mixing the method, for example, pulp, used commonly conventionally and the above-mentioned loading material at a predetermined rate, adding water, a sizing compound,

and a suitable addition ingredient, and milling paper.

[0017]As for the calcium carbonate printing paper of this invention, it is preferred to comprise presentation that the ash which remains with an electric furnace etc. eventually at the time of glow fullness \*\* is set to pH 7-10 40 or less weight %.

[0018]

[Effect of the Invention] The outstanding opacity and whiteness degree are shown without using a titanium dioxide and calcination clay together according to this invention, And the fault at the time of using an independent or spindle type calcium carbonate pillar-shaped type calcium carbonate independent as a loading material, Namely, the fault whose waist of paper opacity is low, or tensile strength is small and is weak is improved, The printing paper (for example, rather than tensile strength, opacity was thought as important relatively and raised) which showed good balance about the demand characteristics as desired paper, and adjusted the grade of this balance can be given, The printing paper which has the outstanding whiteness degree, opacity, and stiffness which are equal to what carried out the amount combination of anticipated use of the titanium dioxide mostly can be given by adding further a small amount of titanium dioxides by request. This calcium carbonate printing paper And coating stencil paper, such as art paper and coat paper, A PPC sheet, a thermal paper, an impact paper, hot printing paper, inkjet printing paper, electrostatic recording paper, It is suitable as Japanese tissue printing paper and rice paper, such as copy stencil paper, such as non-coating print sheets, such as office-use papers, such as magnetic recording paper, upper printing paper, middle-class printing paper, especially back carbon paper which is easy to produce the performance difference of an inner filler, and India paper.

[0019]

[Working example]Next, this invention is not restricted by these examples although an working example explains this invention still in detail. Each physical properties of the sample in an working example and a comparative example were searched for in accordance with a following measuring method or valuation basis.

(1) ingredient [ of Kaminaka ]: -- JIS P8128 -- measurement (2) tensile strength: -- by JIS P8113. measurement (3) breaking length: -- JIS P8113 -- measurement (4) whiteness degree: -- JIS P8123 -- measurement (5) opacity: -- JIS P8138 -- pH:JIS P8133 of measurement (6) Kaminaka -- measurement [0020] reference example calcite system spindle-shaped calcium carbonate (the OKUTAMA KOGYO CO. LTD. make.) TP-121SA and aragonite system pillar-shaped calcium carbonate (the OKUTAMA KOGYO CO. LTD. make, TP-123FS) were mixed to the weight ratios 90:10 and 70:30 or 50:50, and mixed calcium carbonate with the physical properties shown in Table 1 was prepared.

[0021]The independent physical properties of calcite system spindle-shaped calcium carbonate and each aragonite system pillar-shaped calcium carbonate were also shown in Table 1 for comparison. Each physical properties in front are measured by the following method.

- (1) Concentration : measure using an infrared moisture meter.
- (2) Viscosity : measure using a Brookfield viscometer.
- (3) 50% particle diameter : it is based on laser type particle size distribution (50% accumulation particle diameter).
- (4) 325 mesh-sieve passage residue : measure with 325 mesh sieves and wet process.

- (5) Wire abrasion degree : measure with the Nippon Filcon abrasion tester (plastic wire).  
 (6) pH : measure with a glass electrode method.  
 (7) Specific surface area : measure by BET.

[0022]

[Table 1]

炭酸カルシウム	紡錘状/柱状 重量比	濃 度 (%)	粘 度 (cP)	粒 度 分 布 ( $\mu\text{m}$ )	325メッシュ 残 渣 (%)	ワイヤー 摩 耗 (mg)	pH	比表面積 ( $\text{m}^2/\text{g}$ )
A	90/10	28.9	1300	3.7	0.001	26	8.9	8.2
B	70/30	26.5	1150	3.7	0.001	23	8.8	9.0
C	50/50	22.9	950	3.8	0.001	21	8.9	9.7
TP-121SA	100/0	30.7	240	3.7	0.001	29	8.9	7.8
TP-123FS	0/100	18.9	1450	3.9	0.001	14	8.8	11.5

[0023] The working examples 1-3, the comparative example 1 - 2 broad-leaved-tree kraft pulp (350csf), and needle-leaf tree kraft pulp (450csf) to pulp raw material 100 weight section mixed by the weight ratio 7:3. Mixed calcium carbonate A-C 18 weight section and the amount part of anatase type titanium dioxide duplexs which were obtained by the reference example are blended, Furthermore, polyacrylamide 0.02 weight section was added as alkyl ketene dimer 0.2 weight section and a yield improver as cation-ized starch 0.5 weight section and a neutral size agent as a paper reinforcing agent, and India paper was manufactured with the hand papermaking using a square-shaped sheet machine. The physical properties of this thing are shown in Table 2.

[0024] To pulp raw material 100 weight section mixed by the weight ratio 7:3, working-example 4 broad-leaved-tree kraft pulp (350csf) and needle-leaf tree kraft pulp (450csf). 60 weight % of TP-121SA (a trade name, Okutama industrial company make, spindle type calcite system calcium carbonate), 30 weight % of TP-123FSs (a trade name, Okutama industrial company make, pillar-shaped type aragonite system calcium carbonate), and KRONOS-KA10 (a trade name.) Loading material 20 weight section which comprises the Titan Kogyo K.K. make and 10 weight % of anatase type titanium dioxides is added, Furthermore cation-ized starch (paper reinforcing agent) 0.5 weight section, alkali ketene dimer (neutral size agent) 0.2 weight section, and polyacrylamide (yield improver) 0.02 weight section were added, and India paper was manufactured with the hand papermaking using a square-shaped sheet machine. The physical properties of this thing are shown in Table 2.

[0025] India paper was manufactured like the working example 4 except having replaced comparative example 1 loading material with what comprises 80 weight % of TP-121SA, and 1020 weight % of KRONOS-KA. The physical properties of this thing are shown in Table 2.

[0026] Working-example 5 back-carbon paper was manufactured like the working example 4. The physical properties of this thing are shown in Table 2.

[0027] Back carbon paper was manufactured like the working example 5 except having replaced comparative example 2 loading material with what comprises 80 weight % of TP-121SA, and 1020 weight % of KRONOS-KA. The physical properties of this thing are shown in Table 2.

[0028] The loading material which changes from 70 weight % of TP-121SA and 30 weight % of TP-123FSs to working-example 6 flax pulp (80csf) 100 weight section was added, and rice paper was manufactured with the hand papermaking using a square-

shaped sheet machine. The physical properties of this thing are shown in Table 2.

[0029]Rice paper was manufactured like the working example 6 except having replaced comparative example 3 loading material with what comprises only TP-121SA. The physical properties of this thing are shown in Table 2.

[0030]Rice paper was manufactured like the working example 6 except having replaced comparative example 4 loading material with what comprises 95 weight % of TP-121SA, and 105 weight % of KRONOS-KA. The physical properties of this thing are shown in Table 2.

[0031]

[Table 2]

例	坪 量 (g/m <sup>2</sup> )	密 度 (g/cm <sup>3</sup> )	灰 分 (%)	引張強さ (kg)	裂断長 (km)	白 色 度 (%)	不透明度 (%)	pH
実施例 1	31.6	0.43	19.6	1.71	3.61	87.0	85.6	7.3
実施例 2	31.1	0.42	19.3	1.68	3.60	87.2	85.9	7.4
実施例 3	31.4	0.41	19.4	1.59	3.38	87.4	86.1	7.3
実施例 4	31.5	0.43	19.5	1.67	3.53	87.2	85.8	7.3
比較例 1	31.2	0.42	20.0	1.74	3.72	87.6	86.0	7.3
実施例 5	42.9	0.44	19.4	2.01	3.12	87.4	86.9	6.8
比較例 2	43.1	0.45	19.7	2.14	3.31	87.9	87.0	6.9
実施例 6	24.5	0.53	18.6	1.30	3.57	87.4	83.3	8.9
比較例 3	24.3	0.52	18.9	1.38	3.76	87.1	82.9	8.7
比較例 4	24.4	0.52	19.1	1.40	3.81	87.5	83.4	9.0

[0032] From this, the printing paper of this invention of each working example is understood that the balance of optical properties, such as opacity and a whiteness degree, and physical characteristics, such as tensile strength and nerve of paper, is good in the demand characteristics as desired paper. What used only the calcium carbonate mixture of this invention as the loading material when the working example 6 and the comparative examples 3 and 4 were contrasted, If opacity and a whiteness degree excellent also in not using a titanium dioxide together, either are shown and the working example 5 and the comparative example 2 are contrasted for the working example 4 and the comparative example 1 again, even if it makes the loadings of a titanium dioxide a small quantity, The physical properties which are equal to the thing of the conventional usual combination which made these loadings the twice mostly are acquired, pillar-shaped type calcium carbonate can be substituted for an expensive titanium dioxide in part at least, and it turns out that the manufacturing cost of desired paper can be reduced. In the demand characteristics as desired paper from the working examples 1 thru/or 4, By changing the ratio of spindle-shaped calcium carbonate and pillar-shaped calcium carbonate, Optical properties, such as opacity and a whiteness degree, and physical characteristics, such as tensile strength, are fluctuated relatively, For example, it becomes possible to attach greater importance than to tensile strength to opacity like the working example 3, or to attach greater importance than to opacity to tensile strength like the working example 1, and it turns out that the grade of the balance of both the characteristics can be adjusted.

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